Short communication

The effects of O_2 pressure on Li–O_2 secondary battery discharge capacity and rate capability

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HIGHLIGHTS

- A pressurized Li-O_2 system significantly increases the capacity and rate capability.
- Pressurized Li-O_2 can operate at rates comparable to commercial Li-ion cells.
- The optimal pressure (10 atm) does not require a heavier case than Li-ion hard cells.

ARTICLE INFO

ABSTRACT

The nonaqueous lithium–oxygen (Li–O_2) battery is investigated in a contained, high pressure O_2 system. Increasing the O_2 pressure from 1 atm to 10 atm of O_2 increased the discharge potential by 10% when discharged at 100 μA cm^{-2} from 2.65 V to 2.77 V. In addition, the cell discharge capacity increased from 1400 mAh g$_C^{-1}$ at 1 atm of O_2 to 2100 mAh g$_C^{-1}$ at 10 atm at 100 μA cm^{-2}. The discharge capacity of the 1 atm O_2 cell decreased to 100 mAh g$_C^{-1}$ at 1000 μA cm^{-2}, while at 10 atm of O_2 it retained one third of the 100 μA cm^{-2} capacity at 2100 μA cm^{-2} and two thirds the 1 atm/100 μA cm^{-2} capacity at 500 μA cm^{-2}. This increase in capacity results from a more efficient utilization of the carbon electrode surface at higher pressures. As seen by SEM, the thickness of the discharge product layer was much greater when discharged under higher pressures, indicating more O_2 reached the active carbon surfaces and was reduced. In addition, at high pressure the electrode surface was more evenly used, having fewer areas with little or no discharge products.

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1. Introduction

The energy density of practical lithium–air secondary battery systems range from 800 to 3000 Wh kg^{-1} [1,2], up to twelve times the energy density of state of the art Li-ion cells (~200 Wh kg^{-1}). However, it has been shown [3] that common airborne contaminants, water and CO_2, cause irreversible formation of products such as Li_2CO_3 and LiOH, which degrade the electrode activity and sequester O_2. This reduces the capability of the system and poses a challenge to the usability of an open, air-breathing Li–O_2 system. This underscores the necessity for developing a closed Li–O_2 system. In addition to reducing exposure to these contaminants, switching to a closed system allows for extension to air-free systems such as under water, space, or an enclosed system. Pure, high pressure oxygen in a closed, pressurized system should offer added

performance advantages over air. It should increase both the discharge capacity and cell voltage, and have a significant effect on the maximum discharge rate [4,5]. A previous study [4] showed an increase in both capacity and discharge rate, demonstrated an increase in discharge capacity by a factor of five for 10 atm vs. 1 atm O_2 for their device. However, this study was in a propylene carbonate system, which has since been demonstrated [6] to form Li_2CO_3 instead of Li_2O_2 with cycling. The Li_2CO_3 consumes the electrolyte, and thus this study did not address the effects of O_2 pressure on the reversible Li–O_2 system.

This study uses diglyme, an etheric solvent [7], that exhibits some oxidative instability at high potentials [8], but does reversibly produce Li_2O_2 on the cathode and is more suitable for investigation of the effects of O_2 partial pressure on cell performance. This study uses galvanostatic measurements of Swagelok type cells [9] in enclosed, high pressure vessels to evaluate and compare the advantages of using high pressure O_2 to air as a cathode source over a range of discharge rates. The morphology of the discharge products is evaluated for the effects of increasing discharge rates and O_2 concentration. Due to the potential

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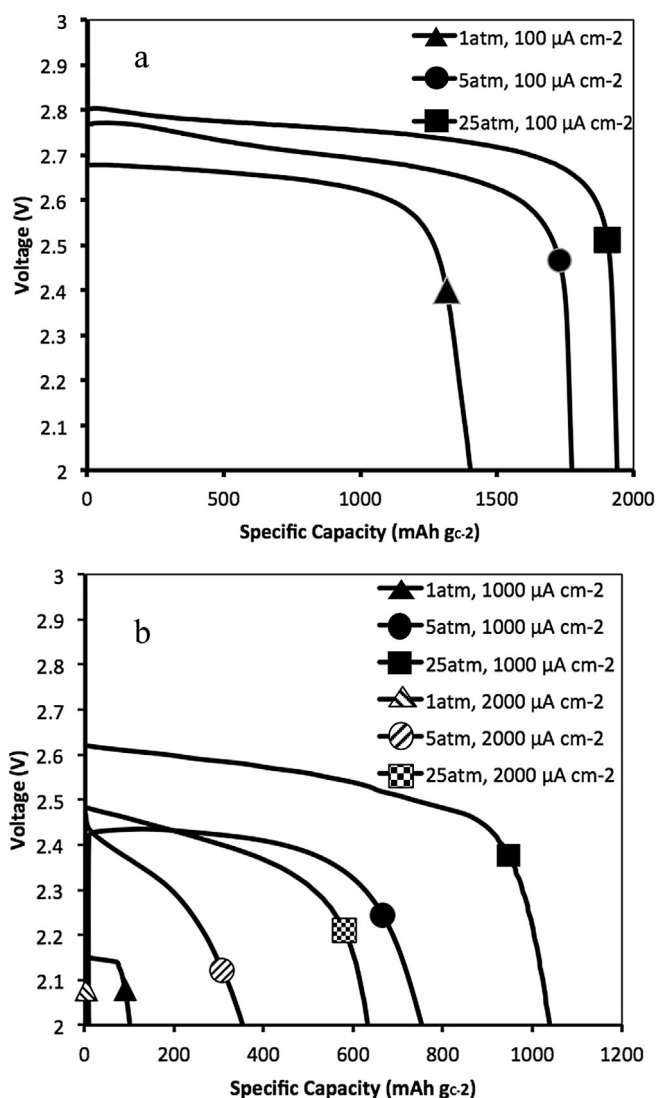*E-mail addresses:* ejoseph.nemanick@aero.org, nemanice@gmail.com (E.J. Nemanick).

Fig. 1. The discharge profiles for carbon electrodes in 1 atm, 5 atm, and 25 atm O_2 at (a) 100 μA cm^{-2} and (b) 1000 and 2000 μA cm^{-2}.

oxidation of the electrolyte and electrode on charging this system [10–13], as well as the questions regarding the effectiveness of catalytic surfaces [14–16], this paper only studies the discharge reaction, and should provide an effective investigation of the advantages of switching to a contained, high pressure Li–O_2 battery system.

2. Experimental

High surface area carbon electrode material was made from Super C65 carbon black (Timcal, BET surface area 62 m^2 g^{-1}) and 10% dry weight of T-30 Teflon water-based emulsion (DuPont). The active material (2.1 mg) was applied to a 0.5 inch type 304 stainless steel (SS) mesh disk and compressed using a roller mill in a dry room (H$_2$O pressure <50 ppm). The experimental cell was a 0.5 inch Swagelok type cell, constructed with a Li disk as the anode and Celgard trilayer separator 2320. A bare SS mesh and an air spring to allow for O_2 flow were placed on top of the electrode. The cell was sealed and filled in the dry room with 80 uL of 0.5 M lithium trifluoromethane sulfonate (triflate, LiTFS, 99.995%, Aldrich) in diglyme (DG, anhydrous, 99.5% Aldrich, dried over molecular sieves), prepared in an Ar glovebox.

The Swagelok cells were placed into high pressure bombs with electrical feedthroughs and flushed with research grade (99.999%) O_2 and brought to the desired pressure, from 1 to 25 atm, while air experiments used the dry room air. Cells were allowed to reach equilibrium with the O_2 environment for 4 h before cycling. Cells were tested on an Arbin Instruments BT2000 battery tester and were discharged from 100 μA cm^{-2} to 2 mA cm^{-2} (67–1340 mA g$_C^{-1}$). Additionally, the discharged electrodes after cell disassembly were examined using a JEOL JSM7600F FE-SEM for morphological characterization.

3. Results and discussion

Despite the interest in using air as an O_2 source, most studies of Li–O_2 chemistry are conducted using pure O_2, already 5× the concentration of O_2 in air. As can be seen in Fig. 1a, the concentration of O_2 in a Li–O_2 cell influences the discharge voltage plateau. In this experiment, the discharge voltage plateau increased by ∼120 mV by increasing the O_2 pressure from 1 atm to 25 atm. This effect should be caused by the combination of a Nernstian

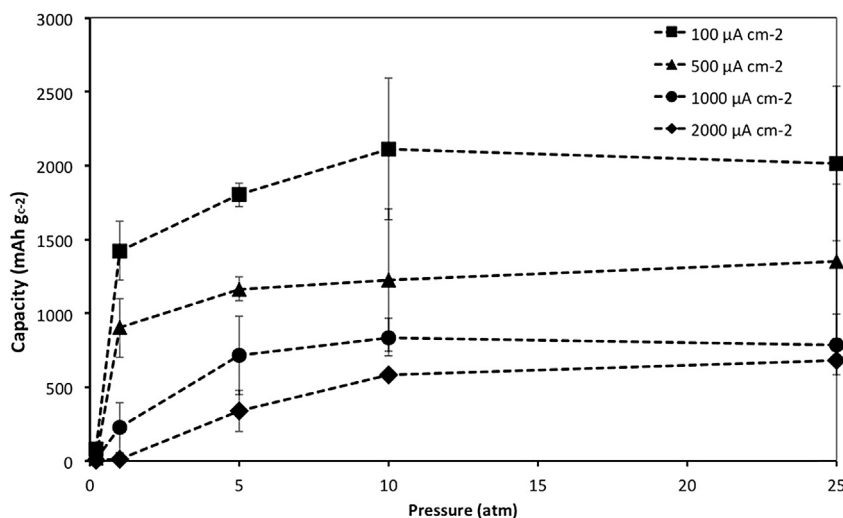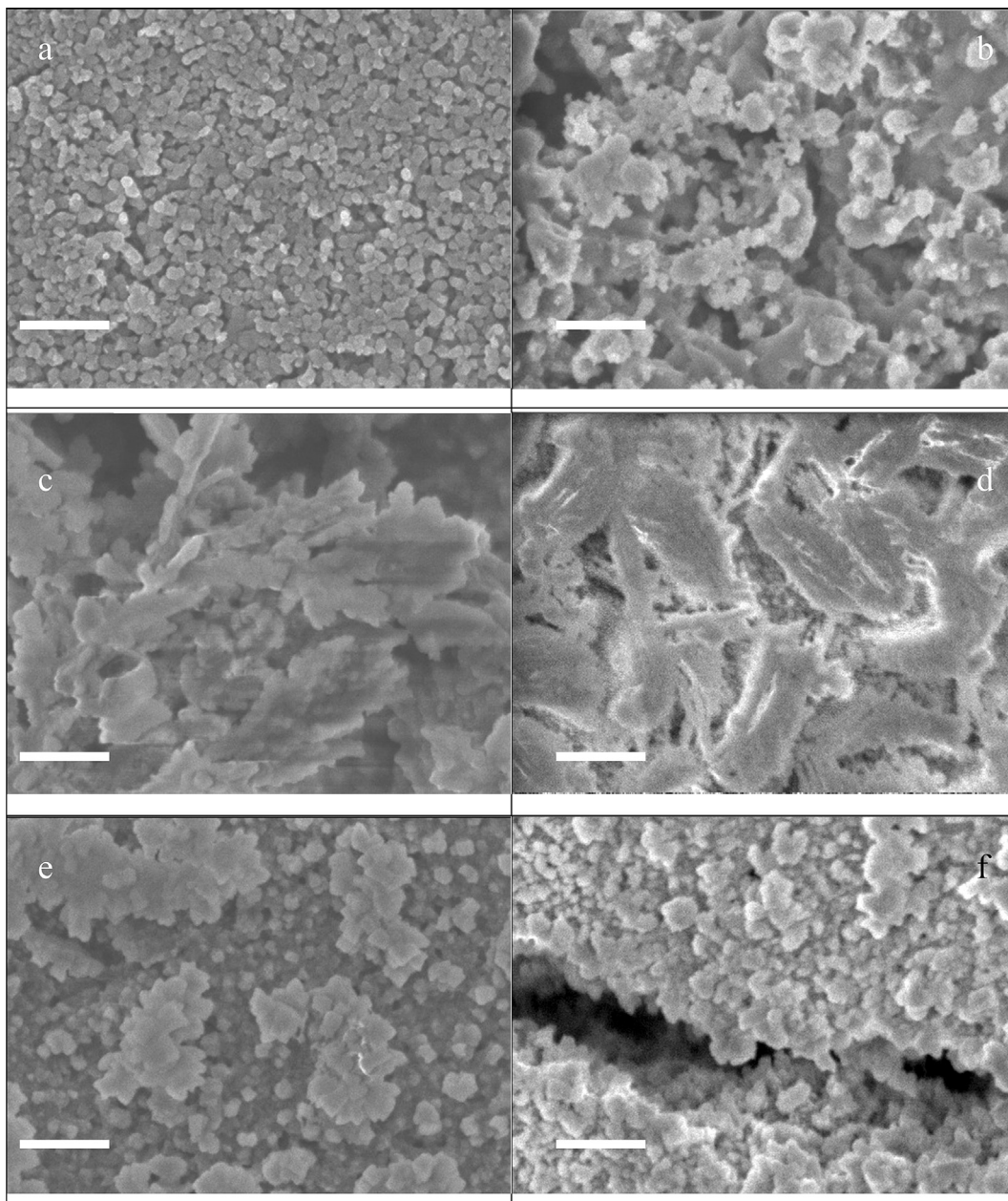**Fig. 2.** The discharge capacities of 2.1 mg electrodes from 100 to 2000 μA cm^{-2}. The air capacities were very low for even 100 μA cm^{-2}, or 67 mA g$_C^{-1}$. The capacities rise steadily from 1 to 10 atm, and then level off for the 25 atm capacity.

Fig. 3. FE-SEM images of the surfaces of the carbon positive electrode. a) is a fresh electrode, and the oxygen facing surface for b) air discharged at 100 μA cm^{-2}, c) 1 atm O$_2$ discharged at 100 μA cm^{-2}, d) 25 atm O$_2$ discharged at 100 μA cm^{-2}, e) 1 atm O$_2$ discharged at 1000 μA cm^{-2}, and f) 25 atm discharged at 1000 μA cm^{-2}. All images are at 50,000× magnification, and the scale bars are equal to 500 nm.

effect, where increasing [O$_2$] increases the potential of the overall reaction at the positive electrode,

$$2Li^+ + O_2 + 2e^- \rightarrow Li_2O_2(s) \qquad (1)$$

and changes in the diffusion controlled impedance of the cell. The impedance will decrease as the diffusion of O$_2$ increases to the electrode surface at higher pressure, which improves the typical rate capability/discharge voltage trade off for batteries. In Fig. 1b the 25 atm/1000 μA cm^{-2} discharge profile retains a significant portion of its low discharge rate voltage, at 2.6 V, while the 1 atm has fallen to 2.15 V at this rate. Even at 2000 μA cm^{-2}, the 25 atm cell still discharges at 2.4 V, while the 1 atm cell does not function. This increase in the discharge voltage represents a significant improvement to the energy density of the cell across all rates.

The discharge capacities of the cell were also strongly influenced by the pressure of O$_2$ and the rate of discharge, as seen in Fig. 2. The maximum discharge capacity at 1000 μA cm^{-2} for 25 atm of O$_2$ is 1030 mAh g$_C^{-1}$, still 55% of the 100 μA cm^{-2} capacity. This significant retention of capacity at this high discharge rate represents a critical improvement in the typically low power capability of the Li−air cell. The capacities for cells using air for this cell design and carbon loading were very low, below 100 mAh g$_C^{-1}$ at 100 μA cm^{-2}.

For all rates in this study, increasing the partial pressure of O$_2$ increased the discharge capacity of the cell. The cell capacity increased from 1390 mAh g$_C^{-1}$ to 2100 mAh g$_C^{-1}$ from 1 to 10 atm O$_2$ at 100 μA cm^{-2}. However, this effect does not appear to be unlimited, as the discharge capacity did not significantly increase between 10 atm and 25 atm O$_2$. This data indicates that ultra high

O_2 pressures are not needed to achieve the maximum discharge capacity for this cell. In addition, while the capacity of the cell declined with increasing rate for all pressures, it declined significantly less for high pressures of O_2. The air cell capacity fell to zero by 500 $\mu A\,cm^{-2}$, but the 25 atm cell approached the capacity of the 1 atm/100 $\mu A\,cm^{-2}$ cell at 500 $\mu A\,cm^{-2}$. The retention of rate capability with increasing O_2 pressure indicates that a limiting parameter for the discharge reaction at the positive electrode is O_2 supply and transport. From this it can be inferred that scaling up the electrode thickness for an air-breathing cell would not improve the capacity without significantly lowering the rate capability, as diffusion to the electrode surface would be unchanged.

Fig. 3a and b shows SEM images of the surfaces of a bare carbon cathode and an electrode discharged at 100 $\mu A\,cm^{-2}$ in air. The Li_2O_2 discharge products can be seen on the carbon surface as bright material in Fig 3b. At 100 $\mu A\,cm^{-2}$ in air, the electrode surface was not heavily covered with discharge products, seen as small white particles on the carbon surface. The discharge product particles appear as small brighter spots on the uncoated particles seen in Fig 3a, indicating an insulating material. The imaged surface is the one facing the air supply, and would have been directly exposed to diffusing O_2. The low apparent coverage correlates well with the discharge capacity for air cells, with no (85 mAh g_C^{-1}) capacity.

In contrast, the 1 atm and 25 atm carbon surfaces discharged at 100 $\mu A\,cm^{-2}$ in Fig. 3c and d show significantly more discharge products. In 1 atm of O_2 the products have begun to grow, forming plate- and leaf-like structures extending from and into the surface of the electrode. Increasing the amount of oxygen to 25 atm changes the broad, high surface area, deposits of discharge products to a dense, filled-in mass of products. Increasing the discharge rate to 1000 $\mu A\,cm^{-2}$ at 1 atm as seen in Fig. 3e creates far less of the discharge products, with open areas of carbon black particles in between stubby Li_2O_2 deposits. These bare areas appear to caused by a lack of O_2 at the surface, as the discharge products on the 1000 $\mu A\,cm^{-2}$ and 25 atm of O_2 surface still appeared dense in Fig. 3f, with a thick coating of discharge products on the surface and no apparent areas where the carbon was left uncovered, as was seen in Fig. 3e. This correlates well with the discharge capacities for these conditions, at 780 and 85 mAh g_C^{-1} respectively. This indicates that for the air electrodes discharged at a high rate, the capacity limiting factor is not the available electrode surface, but rather the O_2 availability.

The nature of the capacity increases with O_2 pressure is then a material utilization effect. At the slowest rates measured in air, there still appeared to be sections of the electrode surface that did not have dense layers of discharge products, while at the same rate the 25 atm O_2 samples appeared very thick and covered the entire electrode surface. This indicates that diffusion of O_2 into the electrode limits performance for low pressure O_2 systems. By increasing the amount of O_2 present, there is more O_2 available within the pores of the electrode for reaction, because diffusion into the electrode pores is more rapid. The macroscopically flat nature of the electrode forces planar diffusion of O_2 to the electrode, and thus causes a limitation on the battery power due to the rate of diffusion of oxygen to the electrode.

4. Conclusion

It has been shown that the discharge capacity and rate capability of the Li−O_2 battery is enhanced by using high pressure O_2. Transitioning from 1 atm up to 10 atm increased the discharge capacity 50% at 100 uA cm^{-2}. At a higher rate, 1000 $\mu A\,cm^{-2}$, which may be required for many applications, these cells had a very low capacity at 225 mAh g_C^{-1} in 1 atm oxygen, while a 10 atm cell still retained 840 mAh g_C^{-1}. The performance of the cell saw diminishing returns for the cell at pressures above 10 atm, with 25 atm cells not showing a significant difference in performance over 10 atm. This may indicate a kinetic limit to the cell or a saturation of oxygen in the electrolyte. It was demonstrated by SEM that the electrode surface is not efficiently used if discharge rates are too high for a given O_2 supply, with large areas of the electrode not having dense layers of discharge products. Increasing the O_2 supply and slowing the discharge rate both increase the surface utilization and discharge product density.

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